

(19)  **Canadian
Intellectual Property
Office**

An Agency of
Industry Canada

**Office de la Propriété
Intellectuelle
du Canada**

Un organisme
d'Industrie Canada

(11) **CA 2 196 349** (13) **C**
(40) 31.10.2000
(43) 01.08.1997
(45) 31.10.2000

(12)

(21) **2 196 349**

(22) **30.01.1997**

(51) Int. Cl. ⁶: **B01J 23/44, C07C 11/02,
C07C 13/02, B01J 37/02,
B01J 21/04, C07C 5/05,
B01J 27/08, B01J 37/08,
C07C 13/61**

(30) **08/595,326 US 01.02.1996**

(73) **PHILLIPS PETROLEUM COMPANY
214 Patent & Library
Building BARTLESVILLE XX (US).**

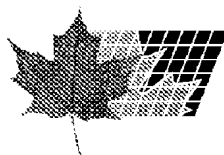
(72) **Cheung, Tin-Tack Peter (US).
Johnson, Marvin M. (US).**

(74) **OSLER, HOSKIN & HARCOURT LLP**

(54) **HYDROGENATION D'HYDROCARBURES ET CATALYSEUR UTILE A CETTE FIN**
(54) **HYDROCARBON HYDROGENATION AND CATALYST THEREFOR**

(57)

A supported hydrogenation catalyst composition consists essentially of a palladium component, at least one alkali metal iodide (preferably KI) and an inorganic support material (preferably Al₂O₃). This catalyst composition is employed in the selective hydrogenation of C₃-C₁₂ diolefins with hydrogen gas to the corresponding monoolefins.



(72) Cheung, Tin-Tack Peter, US

(72) Johnson, Marvin M., US

(73) PHILLIPS PETROLEUM COMPANY, US

(51) Int. Cl.⁶ B01J 23/44, C07C 13/61, B01J 37/08, B01J 27/08, C07C 5/05,
B01J 21/04, B01J 37/02, C07C 13/02, C07C 11/02

(30) 1996/02/01 (08/595,326) US

(54) **HYDROGENATION D'HYDROCARBURES ET CATALYSEUR
UTILE A CETTE FIN**

(54) **HYDROCARBON HYDROGENATION AND CATALYST
THEREFOR**

(57) Composition catalytique sur support pour hydrogénation, renfermant principalement un constituant au palladium, au moins un iodure de métal alcalin (de préférence KI) et une matière minérale de support (de préférence Al₂O₃). Cette composition catalytique est employée pour l'hydrogénation sélective de dioléfines C₃-C₁₂ en monooléfines correspondantes à l'aide de l'hydrogène.

(57) A supported hydrogenation catalyst composition consists essentially of a palladium component, at least one alkali metal iodide (preferably KI) and an inorganic support material (preferably Al₂O₃). This catalyst composition is employed in the selective hydrogenation of C₃-C₁₂ diolefins with hydrogen gas to the corresponding monoolefins.



Abstract

A supported hydrogenation catalyst composition consists essentially of a palladium component, at least one alkali metal iodide (preferably KI) and an inorganic support material (preferably Al_2O_3). This catalyst composition is employed in the selective hydrogenation of $\text{C}_3\text{-C}_{12}$ diolefins with hydrogen gas to the corresponding monoolefins.

2 1 9 6 3 4 9

1

HYDROCARBON HYDROGENATION AND CATALYST THEREFOR**Background of the Invention**

In one aspect, this invention relates to a supported noble metal catalyst composition. In another aspect, this invention relates to a process for selectively hydrogenating diolefins (alkadienes) to monoolefins (alkenes) employing a supported noble metal catalyst composition.

5 Catalysts comprising palladium and a support material are known catalysts for diene and/or acetylene hydrogenation. Even though these catalysts are effective hydrogenation catalysts, there is an ever present need for further improvements (e.g., to achieve enhanced selectivity to monoolefins and/or increased catalyst life.). The present invention is directed to a modified supported palladium
10 catalyst composition and its use in processes for the selective hydrogenation of diolefins (alkadienes) to monoolefins (alkenes). The catalyst composition of this invention is also suited for the selective hydrogenation of acetylenes (alkynes) to the corresponding monoolefins (alkenes).

Summary of the Invention

It is an object of this invention to provide an improved palladium-containing composition (which is useful as a catalyst in the selective hydrogenation of diolefins and/or acetylenes to monoolefins). It is another object of this invention to employ this improved catalyst composition in the selective hydrogenation of diolefins to monoolefins. It is a specific object of this invention to employ this improved catalyst composition in the selective hydrogenation of C₄-C₅ alkadienes to the corresponding C₄-C₅ alkenes. It is another specific object of this invention to employ this improved catalyst composition in the selective hydrogenation of cyclopentadienes to cyclopentene. It is a further specific object of this invention to employ this improved composition in the selective hydrogenation of dicyclopentadiene to at least one dihydrodicyclopentadiene. Other objects and advantages will be apparent from the detailed description and the appended claims.

In accordance with this invention, a catalyst composition is provided which consists essentially of (a) at least one palladium-containing material selected from the group consisting of palladium metal and palladium oxides, (b) at least one alkali metal iodide and (c) at least one inorganic support material. In a preferred embodiment, the alkali metal iodide is potassium iodide and the inorganic support is alumina.

Also in accordance with this invention, an improved process for selectively hydrogenating diolefins containing 3-12 carbon atoms per molecule with hydrogen gas to the corresponding monoolefins containing 3-12 carbon atoms per

molecule is carried out with the catalyst composition of this invention. In a preferred embodiment, the at least one alkadiene is selected from the group consisting of 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene and isoprene are selectively hydrogenated with hydrogen gas to at least one alkene selected from the group consisting of butenes and pentenes in the presence of the catalyst composition of this invention. In another preferred embodiment, 1,3-cyclopentadiene is selectively hydrogenated with hydrogen gas to cyclopentene in the presence of the catalyst composition of this invention. In still another preferred embodiment, dicyclopentadiene is selectively hydrogenated with hydrogen gas to at least one dihydrodicyclopentadiene in the presence of the catalyst composition of this invention.

Brief Description of the Drawings

Figure 1 illustrates the advantages of an invention catalyst over a control catalyst in a selective hydrogenation of diolefins to monoolefins.

Detailed Description of the Invention

The composition of matter of this invention consists essentially of (a) palladium metal and/or at least one palladium oxide, (b) at least one alkali metal iodide (preferably potassium iodide), and (c) an inorganic support material selected from the group consisting of alumina, silica, titania, zirconia, aluminosilicates (clays and/or zeolites), zinc aluminate, zinc titanate, and mixtures of two or more than two of these compounds, preferably alumina, more preferably alpha-alumina. Generally, the catalyst composition contains about 0.01-2 (preferably about 0.05-1) weight-% Pd and about 0.02-10 (preferably about 0.05-5) weight-% alkali metal (preferably K). The catalyst particles can have any suitable shape (spherical, cylindrical, trilobal and the like), and are preferably either spherical pellets or cylindrical extrudates. The

catalyst particles can have any suitable particle size (diameter/length), and generally have a size of about 1-10 mm (preferably about 2-6 mm). The catalyst particles can have any suitable surface area (measured by the BET method by Brunauer, Emmett and Teller employing N_2), and generally have a surface area of about 1-200
5 (preferably about 10-100) m^2/g .

The catalyst particles can be prepared by any suitable means. The promoter components (a) and (b) can be deposited onto and/or incorporated into the inorganic support material by any suitable means and in any suitable order. For instance, the alkali metal iodide can be incorporated into the support material, by
10 impregnation, followed by impregnation of the alkali metal iodide-containing support material with at least one Pd compound (such as H_2PdCl_4), drying and then heating (calcining) of the thus-impregnated composition (preferably in a reducing gas atmosphere such as hydrogen gas, or in an inert gas atmosphere such as nitrogen, helium and the like). Or a supported palladium catalyst composition, preferably a
15 Pd/Al_2O_3 composition (more preferably one which is commercially available, e.g., from Mallinckrodt Specialty Chemicals Company, Erie, PA), can be impregnated with an alkali metal iodide, followed by drying and then heating (preferably in a reducing or inert gas atmosphere) of the thus-impregnated composition. Or the supported
20 palladium catalyst composition can be impregnated with at least one alkali metal iodate, followed by drying and then heating the impregnated material in a reducing gas atmosphere, preferably hydrogen gas (at a temperature sufficient to convert the alkali metal iodate to alkali metal iodide).

The preferred starting material (also referred to as "base catalyst") , which is to be improved in accordance with this invention by incorporation of alkali metal iodide therein, can be any supported palladium-containing composition. The base catalyst composition can be a fresh hydrogenation catalyst or it can be a used and thereafter regenerated hydrogenation catalyst composition. Broadly, the base catalyst can contain about 0.01-2 (preferably about 0.05-1) weight-% Pd, and a solid inorganic support material (listed above), preferably alumina (more preferably alpha-alumina). The supported Pd-containing base catalyst particles can have any suitable shape, and preferably are spherical pellets or cylindrical extrudates. The size of these supported base catalyst particles generally is about 1-10 mm, preferably about 2-6 mm, and its surface generally is about 1-200 m²/g.

In one preferred method of preparing the catalyst composition of this invention, a Pd-containing base catalyst (described above), which more preferably has been prereduced with hydrogen gas at room temperature (about 10-40°C), is contacted with a solution (preferably aqueous) of at least one alkali metal iodide (preferably KI) at such conditions as to obtain a final catalyst composition containing about 0.02-10 (preferably about 0.05-5) weight-% of alkali metal (preferably potassium). Generally, the concentration of the alkali metal iodide in the contacting (impregnating) solution (preferably aqueous) is about 0.02-10 mol/l (preferably about 0.2-3 mol/l). The preferred contacting method is "incipient wetness impregnation", i.e. essentially completely filling the pores of the base catalyst with the alkali metal iodide solution. Generally, the weight ratio of the solution to the solid base catalyst

composition is in the range of about 0.2:1 to about 2:1, preferably about 0.4:1 to about 1:1 (depending on the alkali metal iodide concentration of the impregnating solution and the desired alkali metal iodide level to be attained in the catalyst composition of this invention). Thereafter, the impregnated catalyst composition is substantially
5 dried (preferably at about 50-150°C for about 0.5-20 hours) and heated in a non-oxidizing gas atmosphere (more preferably in a reducing gas such as H₂, or an inert gas such as N₂, He and the like) at a temperature of about 300-600°C (preferably about 300-500°C) for a time period of about 0.2-20 hours (preferably about 1-10 hours).

10 In another preferred method of preparing the catalyst composition of this invention, a Pd-containing base catalyst (described above) is contacted with a solution (preferably aqueous) of at least one alkali metal iodate (preferably KIO₃) at such conditions to obtain a final catalyst composition containing about 0.02-10 (preferably about 0.05-5) weight-% alkali metal (preferably K), wherein the
15 concentration of the alkali metal iodate(s) in the impregnating solution is about 0.02-10 mol/l (preferably about 0.2-3 mol/l). The impregnating procedure is carried out essentially in accordance with the method described above for the impregnation with alkali metal iodide. Thereafter, the impregnated catalyst composition is substantially dried (as described above) and heated in a reducing gas (preferably H₂) at
20 a temperature of about 200-600°C (preferably about 300-500°C) for a time period of about 0.2-20 hours (preferably 1-10 hours) so as to convert said at least one alkali metal iodate to at least one alkali metal iodide.

The catalyst composition of this invention is preferably employed in the selective hydrogenation of diolefins (alkadienes and/or cycloalkadienes) containing 3-12 carbon atoms per molecule to the corresponding monoolefins containing 3-12 carbon atoms per molecule, such as 1,3-butadiene to butenes and/or pentadienes to pentenes. The catalyst composition of this invention can be employed directly in this selective hydrogenation process. However, it is preferred to first treat the catalyst with a reducing gas such as hydrogen, because the optimal operation of the selective hydrogenation does not begin until there has been a substantial reduction of the palladium component. Typically, the reduction is carried out at a temperature in the range of about 10°C to about 100°C for at least 10 minutes (preferably about 1-10 hours).

Non-limiting examples of suitable diolefins containing 3-12 carbon atoms per molecule which can be hydrogenated in the process of this invention include propadiene, 1,2-butadiene, 1,3-butadiene, isoprene, 1,2-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,2-hexadiene, 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, 2-methyl-1,2-pentadiene, 2,3-dimethyl-1,3-butadiene, heptadienes, methylhexadienes, octadienes, methylheptadienes, dimethylhexadienes, ethylhexadienes, trimethylpentadienes, methyloctadienes, dimethylheptadienes, ethyloctadienes, trimethylhexadienes, nonadienes, decadienes, undecadienes, dodecadienes, cyclopentadienes, cyclohexadienes, methylcyclopentadienes, cycloheptadienes, methylcyclohexadienes dimethylcyclopentadienes, ethylcyclopentadienes, dicyclopentadiene, and mixtures of one or two of these

diolefins. Presently preferred diolefins are 1,3-butadiene, pentadienes (such as 1,3-pentadiene, 1,4-pentadiene, isoprene), cyclopentadienes (such as 1,3-cyclopentadiene) and dicyclopentadiene (also known as tricyclo[5.2.1]^{2,6}deca-3,8-diene). These diolefins are selectively hydrogenated to the

5 monoolefins containing the same number of C atoms per molecule as the diolefins, e.g., 1,3-butadiene to 1-butene and 2-butene, 1,3-pentadiene and 1,4-pentadiene to 1-pentene and 2-pentene, isoprene to methyl-1-pentenenes and methyl-2-pentenenes, 1,3-cyclopentadiene to cyclopentene, dicyclopentadiene to dihydrocyclopentadienes (in particular, tricyclo[5.2.1]^{2,6}dec-3-ene), and the like.

10 The diolefin-containing feed for the hydrogenation process of this invention can also contain other hydrocarbons, in particular, monoolefins and aromatic hydrocarbons. Non-limiting examples of such other hydrocarbons which can be present in the feed at a level of at least 30 volume-% include ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, methyl-1-butenes

15 (such as 2-methyl-1-butene), methyl-2-butenes (such as 2-methyl-2-butene), 1-hexene, 2-hexene, 3-hexene, methyl-1-pentenenes, 2,3-dimethyl-1-butene, 1-heptene, 2-heptene, 3-heptene, methyl-1-hexenes, methyl-2-hexenes, methyl-3-hexenes, dimethylpentenes, ethylpentenes, octenes, methylheptenes, dimethylhexenes, ethylhexenes, nonenes, methyloctenes, dimethylheptenes, ethylheptenes,

20 trimethylhexenes, cyclopentene, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, dimethylcyclopentenenes, ethylcyclopentenenes, cyclooctenes, methylcycloheptenes, dimethylcyclohexenes, ethylcyclohexenes,

trimethylcyclohexenes, methylcyclooctenes, dimethylcyclooctenes, ethylcyclooctenes, benzene, toluene, ethylbenzene, styrene, xylenes and the like, and mixtures of two or more than two of these hydrocarbons.

5 The fluid feed (which may be liquid or gaseous at the hydrogenating conditions of this process) generally contains about 0.1-99.9 weight-% of at least one diolefin. The fluid feed can additionally contain other hydrocarbons (at a level of about 0.1-99.9 weight-%), in particular aromatic hydrocarbons, such as benzene, toluene, styrene and ethylbenzene, which may be present at a level of about 50-99 weight-%. However, it is within the scope of this invention to employ feeds which
10 contain about 100% of at least one diolefin, such as substantially pure dicyclopentadiene. Also, the feed can contain small amounts (generally less than about 0.05 weight-%, in particular about 10-400 ppm S) of sulfur compounds (such as H₂S, carbonyl sulfide, carbon disulfide, mercaptans, organic sulfides such as thiophene, organic di-, tri- and tetrasulfides, and the like) as impurities. Carbon
15 monoxide and/or water (generally less than about 0.05 mole-% of each) can also be present as impurities.

The selective diolefin hydrogenation process of this invention is generally carried out by contacting a feed stream containing at least one diolefin and molecular hydrogen with the catalyst of this invention (generally contained in a fixed
20 bed). Generally, about 1-10 (preferably about 1-2) moles of hydrogen are employed for each mole of diolefin present in the feed. The temperature necessary for the selective hydrogenation process of this invention depends largely upon the activity of

the catalyst and the desired extent of diolefin hydrogenation. Generally, reaction temperatures in the range of about 30°C to about 200°C are used. A suitable reaction pressure generally is in the range of about 15 to 2,000 pounds per square inch gauge (psig). The liquid hourly space velocity (LHSV) of the hydrocarbon feed can vary
5 over a wide range. Typically, the space velocity of the feed will be in the range of about 0.5 to about 100 liters of hydrocarbon feed per liter of catalyst per hour, more preferably about 2 to about 60 liters/liter/hour. The hydrogenation process conditions should be such as to avoid significant hydrogenation of monoolefins (formed by hydrogenation of diolefins being initially present in the feed) to saturated
10 hydrocarbons (alkanes, cycloalkanes).

In one of the preferred embodiments of the diolefin hydrogenation process of this invention, a feed stream containing at least one pentadiene (1,3-pentadiene and/or 1,4-pentadiene and/or isoprene) and molecular hydrogen is contacted with the catalyst (generally contained in a fixed bed). Generally, the
15 hydrocarbon feed contains other hydrocarbons, such as C₄+ alkanes (butanes, pentanes, hexanes), C₄+ alkenes (butenes, pentenes, hexenes) and aromatic hydrocarbons (benzene, toluene, ethylbenzene, styrene and the like). This preferred hydrogenation process generally employs about 1-2 moles H₂ per mole pentadiene(s). The reaction temperature necessary for the selective hydrogenation of pentadiene
20 depends largely upon the activity of the catalyst and the desired extent of the pentadiene hydrogenation, and generally is in the range of about 35°C to about 100°C. Generally, the total pressure is in the range of about 50 to 1,000 pounds per

square inch gauge (psig). The liquid hourly space velocity (LHSV) of the hydrocarbon feed can also vary over a wide range. Typically, the liquid hourly space velocity will be about 1 to about 50 liter/liter/hour. The hydrogenation process conditions should be such as to avoid significant hydrogenation of pentenes to pentane.

In another preferred embodiment, dicyclopentadiene is selectively hydrogenated to dihydrodicyclopentadienes, mainly the dicyclopentene containing the double bond in the "3" position (i.e., tricyclo[5.2.1]^{2,6}dec-3-ene). In still another preferred embodiment, 1,3-butadiene is selectively hydrogenated to butenes.

Operating conditions for these embodiments are substantially the same as those described above for the selective hydrogenation of pentadiene(s) to pentenes.

It is within the scope of this invention to employ the catalyst composition in accordance with this invention for the selective hydrogenation of acetylenes (alkynes) containing 2-12 carbon atoms to the corresponding monoolefins (alkenes, also containing 2-12 carbon atoms per molecule). Suitable alkynes include (but are not limited to) acetylene (ethyne, C₂H₂), propyne, 1-butyne, 2-butyne, pentynes, hexynes, phenylacetylene and mixtures thereof). The reaction conditions for the selective alkyne hydrogenation are approximately the same as those described above for the selective hydrogenation of diolefins to monoolefins.

If it is desired to regenerate the catalyst of this invention after prolonged use in a hydrogenation process, this can be accomplished by leaching the spent catalyst with water (so as to dissolve the alkali metal iodide), calcining the

leached catalyst in an oxidizing atmosphere (e.g., in air; at about 500-600°C) to burn off carbonaceous deposits, reimpregnating the calcined catalyst with dissolved alkali metal iodide, and heating it (as is described for the fresh catalyst of this invention).

The following examples are presented to further illustrate this invention and should not be construed as unduly limiting the scope of this invention.

Example I

This example illustrates the preparation of various palladium-containing catalysts and their use in the selective hydrogenation of 1,3-butadiene to butenes.

Catalyst A (Control) was a Pd/Al₂O₃ catalyst of spherical shape, which had been provided by the Calsicat Catalyst Division of Mallinckrodt Specialty Chemicals Company, Erie, PA under the product designation "E-143 SDU". This catalyst had a BET/N₂ surface area of 35 m²/g, and a particle size of 1/16 inch. Catalyst A contained 0.3 weight-% Pd.

Catalyst B (Control) was a Pd/Ag/KF/Al₂O₃ catalyst. It was prepared as follows: 80.23 grams of Catalyst A were soaked in an aqueous solution of 4.05 grams of AgNO₃ in 72.7 grams of distilled H₂O for about 1.5 hours. Excess liquid was drained from the Ag-impregnated catalyst, which was then dried at 180°F overnight and calcined for 3 hours at 370°C in air. A sample of 20.18 grams of this calcined Pd/Ag/Al₂O₃ catalyst (labeled "Catalyst X") was then soaked with a solution of 0.47 g potassium fluoride in 14.1 cc of H₂O, while occasionally stirring the mixture. The thus-obtained KF-impregnated Pd/Ag/Al₂O₃ catalyst was dried for

several hours at 180°F and calcined in air at 370°C for 4 hours. Catalyst B contained about 0.28 weight-% Pd, about 1.6 weight-% Ag, and about 1.5 weight-% K (as KF).

5 Catalyst C (Control) was a Pd/Ag/KI/Al₂O₃ catalyst. It was prepared by prereducing 20.15 grams of Catalyst X (described above) for about 1 hour with H₂ gas at room temperature. Thereafter, the H₂-treated catalyst material was soaked at room temperature with a solution of 0.89 g potassium iodide in about 12.0 g distilled water. The KI-impregnated catalyst material was dried at room temperature and heated for 5 hours in nitrogen gas at 400°C. Catalyst C contained about 0.28 weight-% Pd, about 2.6 weight-% Ag and about 1.0 weight-% K (as KI).

10 Catalyst D (Invention) was a Pd/KI/Al₂O₃ catalyst. It was prepared by prereducing 20.6 grams of Catalyst A for about 0.5 hours in a hydrogen gas stream at room temperature, and then soaking the prereduced material with a solution of 0.87 gram potassium iodide in 12.8 grams of water. The KI-impregnated catalyst material was dried over night at room temperature and then heated for about 24 hours in
15 nitrogen gas at 400°C. Catalyst D contained about 0.3 weight-% Pd and about 1.0 weight-% K (as KI). It contained no Ag.

Example II

Catalysts A-D (described above) were tested in the selective hydrogenation of 1,3-butadiene by the following procedure. About 20 cc of each
20 catalyst was placed into a stainless steel reactor tube having an inner diameter of 0.5 inch and a length of about 18 inches. Thermocouples were inserted into the top and bottom regions of the catalyst bed, which was heated by an external furnace. The

hydrocarbon feed was liquid and contained about 79 weight-% 1,3-butadiene, about 13 weight-% of various butenes, about 6 weight-% butanes (mainly n-butane), about 0.3 weight-% 1,2-butadiene, about 0.2 weight-% 1-butyne and about 1.5 weight-% vinylacetylene. The liquid feed rate was about 1 cc/minute in all tests. Hydrogen gas

5 was fed with the liquid hydrocarbon feed so as to provide a H_2 /butadiene mole ratio of about 1:1. The total pressure in the reactor was maintained at about 500 psig, and the average reaction temperature was in the range of about 100°F to about 120°F.

Generally, a portion of the reaction product was recycled to the inlet of the reactor so as to provide a volume ratio of recycle stream to fresh feed stream of about 33:1. The

10 non-recycled product gas was analyzed at various time intervals (generally at intervals of about 1-3 hours) by means of a gas chromatograph. Pertinent test results (obtained after a steady state of the reaction was attained) are summarized in Table I.

TABLE I

Feed	Catalyst	Average Weight Percentage of Compounds in Feed					
		1,3-Butadiene	1-Butene	Cis-2-Butene	Trans-2-Butene	n-Butane	C ₆ +Hydrocarbons
Feed I (for Runs 1-4)		78.8	7.6	2.2	2.8	6.2	0.06
Feed II (for Runs 5-6)		79.1	7.4	2.2	2.7	6.1	0.14

Test Run	Catalyst	Average Weight Percentage of Compounds in Product					
		1,3-Butadiene	1-Butene	Cis-2-Butene	Trans-2-Butene	n-Butane	C ₆ + Hydrocarbons
Run 1 (Control)	A (Pd/Al ₂ O ₃)	7.0	53.2	5.4	27.2	6.8	0.32
Run 2 (Control)	B (Pd/Ag/KF/Al ₂ O ₃)	7.5	51.7	6.6	25.4	8.4	0.30
Run 3* (Control)	C (Pd/Ag/KI/Al ₂ O ₃)	60.4	19.8	3.3	9.4	6.4	0.28
Run 4 (Invention)	D (Pd/KI/Al ₂ O ₃)	5.0	50.9	6.5	29.3	7.9	0.17
Run 5 (Control)	A (Pd/Al ₂ O ₃)	3.3	52.4	6.9	28.6	8.1	0.40
Run 6 (Invention)	D (Pd/KI/Al ₂ O ₃)	3.9	50.9	6.6	30.5	7.6	0.20

*No product recycle was carried out

Test data in Table I show that Invention Catalyst D consistently performed better than control Catalysts A-C, as evidenced by lower yields of "heavies" (C_6+ hydrocarbons, i.e., hydrocarbons containing at least 6 carbon atoms per molecule), which tend to accumulate on the catalyst surface and contribute to the gradual deactivation of the catalyst.

Example III

This example illustrates the selective hydrogenation of dicyclopentadiene to dihydrodicyclopentadiene in the presence of various alumina-supported palladium catalysts (described in Example I).

Hydrogenation tests were carried out as follows. A stainless steel reactor tube (total length: about 18 inches; inner diameter: 0.5 inch) was filled with a bottom layer of about 20-30 cc of "36-grit" Alundum® (alumina having a surface area of less than $1 \text{ cm}^2/\text{g}$), a middle layer of about 20 cc of a particular Pd-containing catalyst, and a top layer of about 20-30 cc of "36-grit" Alundum®. Glass wool was placed below each of the two Alundum ® layers and the catalyst layer. Each employed catalyst was activated by passing hydrogen gas (flow rate: 100 cc H_2 per minute) for 2 hours through the reactor at a temperature of 100°F. Thereafter, a solution of 10 weight-% dicyclopentadiene (DCP) in cyclohexane was introduced (in a downflow mode) into the reactor at a rate of about 1 cc per minute, together with hydrogen gas as cofeed. The H_2 flow rate generally ranged from about 10 cc/minute to about 50 cc/minute, and the reaction temperature generally ranged from about 100°F to about 150°F. No product recycle was carried out. The liquid product

effluent (i.e., the cyclohexane-diluted product) was analyzed by means of a gas chromatograph at various time intervals (generally at 0.5-1 hour intervals). Pertinent test data are summarized in Table II.

TABLE II

Run	Catalyst	Reaction Temp. (°C)	H ₂ Flow Rate (cc/min)	Average Content (Wt-%) of Compound in Reactor Effluent		
				Dicyclopentadiene	Dihydro-dicyclopentadiene	Tetrahydro-dicyclopentadiene
7 (Control)	A (Pd/Al ₂ O ₃)	133 143	45 45	0.05	0.2	9.0
				0.15	0.5	9.4
8 (Control)	B (Pd/Ag/KF/Al ₂ O ₃)	114	30	0.06	2.2	6.2
9 (Invention)	D (Pd/KI/Al ₂ O ₃)	107	30	1.9	4.0	3.4
		107	45	1.9	4.1	3.1
		132	45	0.9	4.3	3.3
		142	45	0.8	4.4	3.3
10 (Control)	A* (Pd/Al ₂ O ₃)	107	25	0.03	0.3	7.3
11 (Invention)	D* (Pd/KI/Al ₂ O ₃)	103	30	0.9	8.6	0.3
		125	45	1.0	8.3	0.3
		145	50	0.2	8.3	0.5

*Catalyst was soaked for about 16 hours at room temperature in gasoline containing about 30 ppm sulfur (mainly thiophene), and was dried before the test.

Test data in Table II show that in Run 9 which employed invention Catalyst D, the yield of the desired dihydrodicyclopentadiene was much higher than in Runs 7 and 8 employing control Catalysts A and B. When invention Catalyst D had been treated with sulfur compounds, before it was used for the hydrogenation of dicyclopentadiene, the selectivity to dihydrodicyclopentadiene was even higher than that achieved with untreated Catalyst D (Run 11 vs. Run 9), whereas the sulfur-treated Catalyst A was still far inferior in terms of selectivity to dihydrodicyclopentadiene (Run 10).

Example IV

In this example, the production of additional Pd/Al₂O₃-containing catalysts is described.

Catalyst A1 (Control) was essentially the same as Catalyst A (Pd/Al₂O₃, described in Example I,) except that Catalyst A1 contained about 0.5 weight-% Pd (in lieu of 0.3 weight-% Pd). It was supplied by the Calsicat Catalyst Division of Mallinckrodt, Specialty Chemicals Company, Erie, PA, under the product designation "E-144 SDU".

Catalyst B1 (Control) was essentially the same as Catalyst B (Pd/Ag/KF/Al₂O₃, described in Example I) except that it contained about 0.5 weight-% Pd (in lieu of about 0.3 weight-% Pd). It was prepared substantially in accordance with the method described for Catalyst B, except that Catalyst A1 was used as the starting material (in lieu of Catalyst A). Catalyst B1 contained about 0.5 weight-% Pd, about 2.6 weight-% Ag and about 2.6 weight-% K.

Catalyst B2 (Control) was a Pd/KF/Al₂O₃ catalyst containing about 0.5 weight-% Pd and about 2.5 weight-% K. It was essentially the same as Catalyst B1, except that no silver was present. It was prepared by impregnating 20.6 grams of Catalyst A1 (Pd/Al₂O₃; described above) with a solution of 0.75 grams of potassium fluoride in 12.0 grams of water, followed by drying overnight at 71 °C (160 °F) and calcining for 2 hours at 380 °C.

Catalyst C1 (Control) was essentially the same as Catalyst C (Pd/Ag/KI/Al₂O₃ described in Example I) except that Catalyst C1 contained about 0.5 weight-% Pd (in lieu of 0.3 weight-% Pd). It was prepared essentially in accordance with the preparation method for Catalyst C except that Catalyst A1 (in lieu of Catalyst A) was used for preparing the starting material (labeled "Catalyst X1"), which was then used to make Catalyst C1. Catalyst C1 contained about 0.5 weight-% Pd, about 2.6 weight-% Ag and about 1.6 weight-% K.

Catalyst D1 (Invention) was a Pd/KI/Al₂O₃ catalyst (similar to Catalyst D, described in Example I). Catalyst D1 was prepared by prereducing 40.3 g of Catalyst A1 for about 40 minutes in a hydrogen stream at room temperature, impregnating the prereduced material with a solution of 1.50 g of potassium iodide in 24.0 g distilled H₂O, drying the KI-impregnated material at room temperature, and heating it in a nitrogen stream at 380 °C for about 4 hours. Catalyst D1 contained about 0.5 weight-% Pd, about 0.7 weight-% K and about 2.1 weight-% I.

Catalyst D2 (Invention) was essentially the same as Catalyst D1, except that 0.67 g KI was used (in lieu of 1.50 g KI) and the final heating of the

Pd/KI/Al₂O₃ material was carried out for 3 hours in hydrogen gas at 400°C (rather than in N₂ at 380°C).

Catalyst D3 (Invention) was a Pd/KI/Al₂O₃ which was prepared using KIO₃ instead of KI. A sample of 40.3 grams of Catalyst A1 was soaked for about 45 minutes with a solution of 0.45 g potassium iodate in 21.7 g water. The KIO₃-impregnated Pd/Al₂O₃ material was dried for several days at 180°F and was then treated for 4 hours in a hydrogen gas stream at 404°C (so as to substantially reduce KIO₃ to KI). Catalyst D3 contained about 0.5 weight-% Pd and about 0.2 weight-% K.

10

Example V

This example illustrates the selective hydrogenation of C₃+ diolefins (contained as minor components in aromatic-rich pyrolysis gasoline) employing catalysts described in Example IV.

The feeds employed in the following hydrogenation tests were refinery streams (from an ethane pyrolysis reactor) called "debutanized aromatic concentrate" (DAC). Approximate compositions of three feeds are listed in Table III.

15

TABLE III

<i>Compound</i>	<i>Weight Percentage of Compounds</i>		
	<i>Feed III</i>	<i>Feed IV</i>	<i>Feed V</i>
1-Pentene	0.9	1.2	2.6
2-Pentene	0.2	0.3	0.7
Isoprene	0.9	2.0	3.7
1,3-Pentadiene	0.9	1.5	3.1
1,4-Pentadiene	0.3	0.6	1.1
1,3-Cyclopentadiene	1.4	2.1	2.7
Cyclopentene	0.9	1.4	2.8
Benzene	73.3	67.7	54.0
Toluene	4.4	1.4	11.2
Ethylbenzene	0.3	<0.1	0.7
Styrene	1.7	2.1	3.0
Dicyclopentadiene	7.6	9.0	0.2
Heavies	1.3	1.7	0.2
Sulfur	~*	~0.001	0.01
<i>Note:</i> Feed V was a light (overhead) DAC fraction from which dicyclopentadiene and heavies had been substantially removed (by fractional distillation).			
*Not determined (estimated to be 0.002-0.005 weight-% S).			

The above-described feed was hydrogenated substantially in accordance with the procedure described in Example II, except that no product recycle was carried out. The temperature and the hydrogen flow were adjusted to hydrogenate about 80% of styrene contained in the feed (mainly to ethylbenzene), so as to operate tests employing different catalysts at conditions of comparable hydrogenation severity. Generally, the reaction temperature was about 120-250°F, the reaction pressure was about 350-500 psig, and the H₂ flow rate was about 25-125

cc/minute. The cooled liquid reactor effluent was analyzed by means of a gas chromatograph. Pertinent test data are summarized in Table IV.

Table IV

Run	Catalyst	Feed	Average Weight Percentage of Component in Feed Product ¹						
			Aliphatic Pentadienes	Aliphatic Pentenes	1,3-Cyclopentadiene	Cyclopentene	Dicyclopentadiene	Dihydrodicyclopentadiene	Tetrahydrodicyclopentadiene
12 (Control)	A1 (Pd/Al ₂ O ₃)	III	~0	2.0	0.1	0.4	1.2	4.2	2.5
13 (Control)	C1 (Pd/Ag/KF/Al ₂ O ₃)	III	~2	~2	~2	~2	~2	~2	~2
14 (Invention)	D1 (Pd/KI/Al ₂ O ₃)	III	<0.1	2.5	<0.1	0.9	0.2	8.0	0.4
15 (Control)	B1 (Pd/Ag/KF/Al ₂ O ₃)	IV	0.1	4.0	0.2	1.0	2.1	6.0	1.4
16 (Control)	B2 (Pd/KF/Al ₂ O ₃)	IV	0.1	3.7	0.1	0.8	1.8	5.8	2.2
17 (Invention)	D1 (Pd/KI/Al ₂ O ₃)	IV	0.1	4.7	<0.1	1.7	0.6	8.5	0.4

¹Product formed at reaction conditions selected to achieve ~80% conversion of styrene (to ethylbenzene).²Catalyst was not active enough to achieve 80% conversion of styrene.

Test data in Table IV clearly show that Runs 14 and 17 employing invention Catalyst D1 ($\text{Pd/KI/Al}_2\text{O}_3$) produced the desired monoolefins (aliphatic pentenes, cyclopentene and dihydrodicyclopentadiene) at higher yields than runs employing control catalysts. Thus, the invention catalyst exhibited higher selectivity to monoolefins than various Pd-containing control catalysts.

Results of three additional test runs (not included in Table IV) employing Feed V and operating at such conditions as to achieve a styrene conversion of 90-95% indicated that invention Catalysts D2 and D3 (described in Example IV) achieved almost complete conversions of aliphatic pentadienes to pentenes and of cyclopentadienes to cyclopentene, whereas control Catalyst A1 was considerably less selective to the C_5 monoolefins.

Results of two month-long comparative tests for hydrogenating a prefractionated debutanized aromatic concentrate (DAC), which was similar to Feed V, employing an invention catalyst and a control catalyst are shown in FIG. 1. In both tests, the feed contained about 2.3-2.5 weight-% aliphatic C_5 monoolefins and about 5.7-5.9 weight-% aliphatic C_5 diolefins. The graphs in FIG. 1 demonstrate that the invention catalyst ($\text{Pd/KI/Al}_2\text{O}_3$, essentially the same as Catalyst D2) was considerably more selective to C_5 monoolefins than a corresponding control catalyst ($\text{Pd/Al}_2\text{O}_3$, essentially the same as Catalyst A1), and exhibited excellent stability over a time period spanning from the fifth day to the thirtieth day of the hydrogenation reaction. Both tests were run at such conditions as to attain approximately the same styrene conversion (about 92-95%). At these conditions, essentially complete

conversion of all aliphatic C₅ diolefin was achieved. The most pertinent reaction conditions of the run employing the invention catalyst (Pd/KI/Al₂O₃) were: reaction temperature of 170-210°F, reaction pressure of 340-360 psig, DAC feed rate of 0.9-1.1 cc/minute, and H₂ feed rate of 65-75 cc/minute. A portion of the reaction product was recycled to the inlet of the reactor so as to provide a volume ratio of recycle stream to fresh feed stream of about 1:1.

Reasonable variations, modifications and adaptations for various usages and conditions can be made within the scope of the disclosure and the appended claims, without departing from the scope of this invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composition of matter consisting essentially of (a) at least one palladium containing material selected from the group consisting of palladium metal and palladium oxides, (b) at least one alkali metal iodide, and (c) at least one inorganic support material, wherein said composition comprises 0.01 to 2 weight % palladium and 0.02 to 10 weight % alkali metal.
2. A composition in accordance with claim 1, wherein said at least one alkali metal iodide is potassium iodide.
3. A composition in accordance with claim 1 wherein said at least one inorganic support material is alumina.
4. A composition in accordance with claim 1, wherein said at least one alkali metal iodide is potassium iodide and said at least one inorganic support material is selected from the group consisting of alumina, silica, titania, zirconia, aluminosilicates, zinc aluminate, zinc titanate, and mixtures thereof.
5. A composition in accordance with claim 4, containing 0.05-1 weight-% palladium and 0.05-5 weight-% potassium, and having a surface area of about 1-200 m²/g; and said at least one inorganic support material is alumina.
6. A composition in accordance with claim 1, having been prepared by a method comprising the steps of contacting a material consisting essentially of

component (a) and component (c) with a solution of at least one alkali metal iodide, drying the obtained alkali metal iodide-impregnated material, and heating the obtained dried material in a non-oxidizing gas atmosphere at a temperature of 300-600°C for a time period of 0.2-20 hours.

7. A composition in accordance with claim 6, wherein said component (c) is alumina and said at least one alkali metal iodide is potassium iodide.

8. A composition in accordance with claim 1, having been prepared by a method comprising the steps of contacting a material consisting essentially of component (a) and component (c) with a solution of at least one alkali metal iodate, drying the obtained alkali metal iodate-impregnated material, and heating the obtained dried material in a reducing gas at a temperature of 200-600°C for a time period of 0.2-20 hours, so as to convert said at least one alkali metal iodate to at least one alkali metal iodide.

9. A composition in accordance with claim 8, wherein said component (c) is alumina and said at least one alkali metal iodate is potassium iodate.

10. In a process for selectively hydrogenating diolefins containing 3-12 carbon atoms per molecule with hydrogen gas to monoolefins containing 3-12 carbon atoms per molecule, the improvement which comprises employing a

catalyst composition consisting essentially of (a) at least one palladium containing material selected from the group consisting of palladium metal and palladium oxides, (b) at least one alkali metal iodide, and (c) at least one inorganic support material, wherein said composition comprises 0.01 to 2 weight % palladium and 0.02 to 10 weight % alkali metal.

11. A process in accordance with claim 10, wherein said at least one inorganic support material is selected from the group consisting of alumina, silica, titania, zirconia, aluminosilicates, zinc aluminate, zinc titanate, and mixtures thereof.

12. A process in accordance with claim 10, wherein said at least one alkali metal iodide is potassium iodide, and said at least one inorganic support material is alumina.

13. A process in accordance with claim 10, wherein said catalyst composition contains 0.05-1 weight-% palladium and 0.05-5 weight-% potassium, and has a surface area of 1-200 m²/g; and said at least one inorganic support material is alumina.

14. A process in accordance with claim 10, wherein said at least one diolefin is selected from the group consisting of 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, isoprene, 1,3-cyclopentadiene, and dicyclopentadiene.

15. A process in accordance with claim 14, wherein said at least one diolefin is contained in a feed which additionally contains 50-99 weight-% of aromatic hydrocarbons.

16. A process in accordance with claim 10, wherein the reaction temperature is 30-200°C and the reaction pressure is 15-2000 psig.

17. A process in accordance with claim 16, wherein 1-2 moles of hydrogen are employed for each mole of said at least one diolefin present.

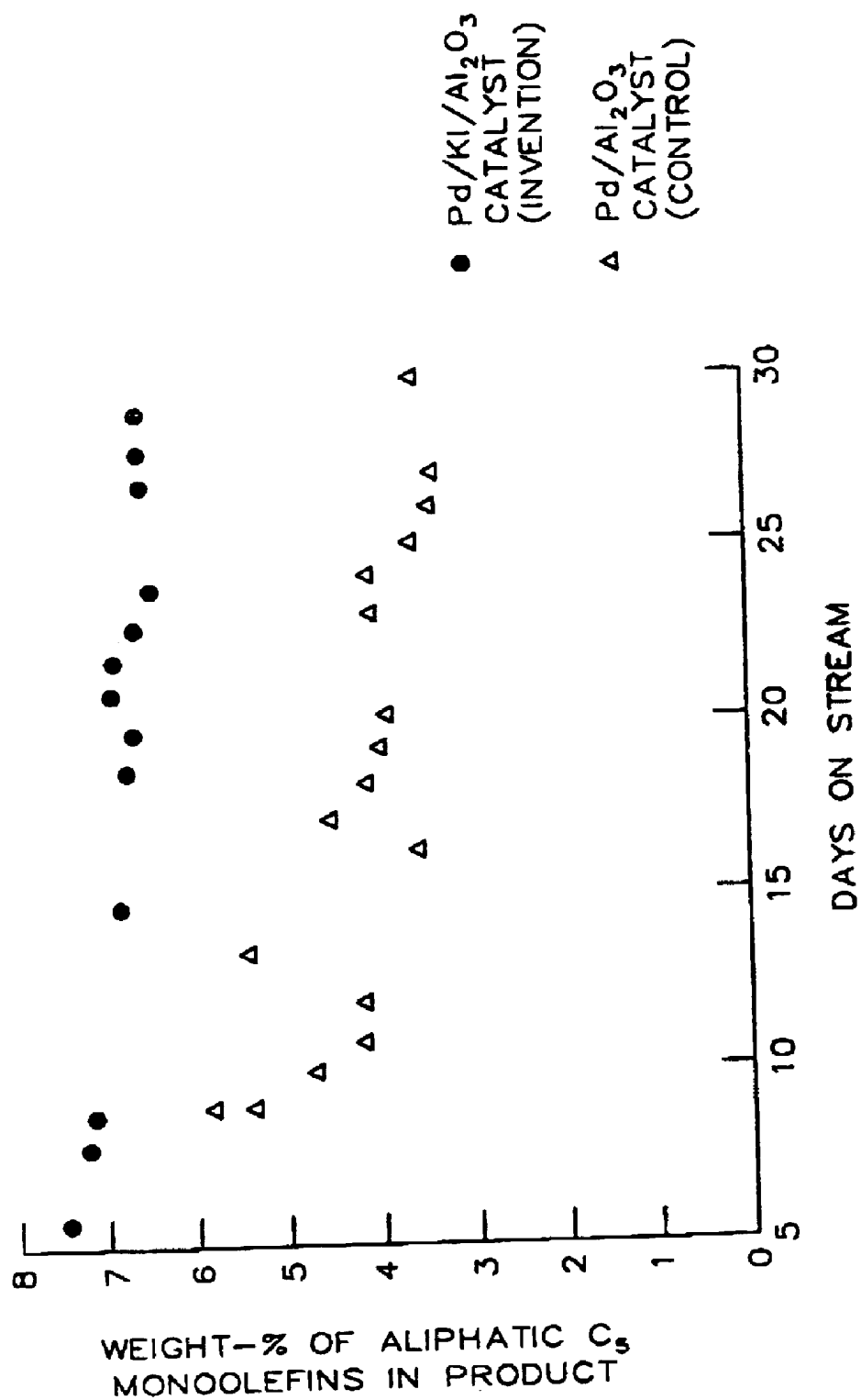


FIG. 1